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10,000 YEARS OF ATMOSPHERIC CHEMISTRY
AT DYE 3, GREENLAND

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10,000 Years of Atmospheric Chemistry at Dye 3, Greenland

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Abstract

Measurements of the chemical composition (Cl^- , NO_3^- , SO_4^{2-} and H^+) of ice core samples from Dye 3, Greenland show that recent increases in the concentration of nitrate and sulfate have occurred which can be attributed to anthropogenic sources. These anthropogenic sources have changed not only the magnitude of impurity levels in Greenland snow, but also the seasonal pattern of impurity concentration. The observed change in seasonal deposition patterns between preindustrial and industrial times is used to analyze the sources of both natural and anthropogenic impurities in Greenland.

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Introduction

Polar ice sheets contain in their trace impurities a record of atmospheric chemistry extending to at least 100 ka BP. A number of investigators have pointed out the existence of variations in this record over a wide range of time scales [1-7]. Although it is clear that these variations reflect changes in past environments, the complexity of the global atmospheric system makes it very difficult to interpret changes in snow chemistry directly in terms of past environmental changes. The possible mechanisms affecting snow composition are both global (changes in natural geochemical fluxes, changes in global atmospheric circulation) and local (changes in snowfall rate, changes in temperature, input of volcanic material). In the twentieth century anthropogenic inputs joined the list of influences on Greenland precipitation [1,7]. In order to provide information about the role of transport, we have made a detailed comparison of pre-industrial and industrial impurity concentrations. In this work we show that anthropogenic sources have changed not only the magnitudes of impurity levels in snow, but also the seasonal pattern of impurity concentration.

Experimental

Samples for this study were obtained from a 174 m core drilled at the Dye 3-4B site in south Greenland (65°11' N, 43°49' W), about 5.1 km upflow from the location of the 2037 m core drilled at Dye 3 in 1981. The samples discussed here cover a time period before the 1961 construction of the Dye 3 radar station and therefore we need not be concerned with possible local contamination from this source. The annual mean accumulation rate at Dye 3 4B is 52.7 cm of ice eq. = 0.48 m.w.e. (meters of water equivalent) for the last 200 years as determined by counting seasonal variations in $\delta^{18}O$. Cores were cut in a -15°C cold room to a length approximating 8 samples per year for $\delta^{18}O$ and 10 samples per year for chemical analysis. Oxygen isotope

analyses were performed directly on melted samples using the mass spectrometer at the University of Copenhagen. Samples for chemical analysis were first cleaned to remove surface contamination picked up during coring and shipment. Ice from the two deeper intervals was cleaned by washing with ultrapure water (18 Mohm-cm) in a class 100 clean room. Firn from the two shallower depth intervals was too porous to be washed and was therefore cleaned by mechanically shaving away the outer surfaces of each sample using a stainless steel microtome knife. All preparation of firn samples was done in a laminar flow clean station located in the cold room at SUNYAB. Chloride, nitrate and sulfate were analysed by ion chromatography. Blank values ($\text{Cl}^- = 3$ ppb, $\text{NO}_3^- = 4$ ppb, $\text{SO}_4^{2-} = 2$ ppb) were determined by processing frozen ultrapure laboratory water in the same manner as the actual ice and firn samples. H^+ was determined by measuring the conductivity of the solid ice in the field at -16°C on freshly drilled ice cores [8].

Chemical concentrations, H^+ and $\delta^{18}\text{O}$ for the four depth intervals studied are given in Figure 1. Maxima in the $\delta^{18}\text{O}$ curve indicate summer deposition and minima, winter. In the discussion which follows we refer to the four depth intervals according to the time when they were deposited as 1770's, 1820's, 1920's and 1950's.

Comparison with Conductivity Record

In figure 2 we have plotted both the experimental H^+ , determined as described in [8], and the calculated H^+ . The calculated value for H^+ was determined by assuming that the Cl^- is of marine origin, that marine Cl^- and SO_4^{2-} are accompanied by counter ions other than H^+ and that the $\text{SO}_4^{2-}/\text{Cl}^-$ mass ratio in the marine component is equal to that of seawater, 0.14.

Therefore $\text{H}^+_{\text{calc}} = \text{NO}_3^-/62 + [\text{SO}_4^{2-} - 0.14*\text{Cl}^-]/48$, where H^+_{calc} is in $\mu\text{eq/kg}$

and NO_3^- , SO_4^{2-} and Cl^- are in $\mu\text{grams/kg}$. This model will overestimate H^+ if the non-marine component contains counterions other than H^+ , such as, for example, NH_4^+ . The model will underestimate H^+ if there is an important input of HCl , such as might occur following a volcanic eruption. Because the marine component of SO_4^{2-} is in general small, errors introduced by deviation of the marine $\text{SO}_4^{2-}/\text{Cl}^-$ ratio from 0.14 are not significant in most cases. During the 1770's and 1820's the measured and calculated values agree very well in general, suggesting that the model does a good job of accounting for the ionic balance. In the 1920's and 1950's the calculated H^+ often exceeds the measured H^+ indicating the increase in nitrate and sulfate concentration has been accompanied by an increase in cations in addition to H^+ . Fig. 2 shows clearly that quantitative trends in H^+ can be studied by this technique.

Melt Effects

Melt features are plotted on Fig. 1, allowing an estimate of the effect of melting on the chemical stratigraphy to be made. The DIMs and SIMs (see Figure 1 for melt feature definitions) correlate well with the NO_3^- . Because there are many cases where a summer NO_3^- peak is not accompanied by a melt feature this probably only indicates that nitrate concentrations peak during the warm season. There is no clear evidence from these data for the influence of melting on the chemical stratigraphy at Dye 3 except for a few cases of minor peak broadening although our experience has shown that occasional very large nitrate peaks are associated with melt layers.

Anthropogenic Effects on Ion Concentration

Using $\delta^{18}\text{O}$ to define the annual layers, we calculated mean annual concentrations for Cl^- , NO_3^- , SO_4^{2-} and H^+ . Averages were calculated on a winter to winter interval ($\delta^{18}\text{O}$ minimum to $\delta^{18}\text{O}$ minimum). Years with a clear volcanic input (1766, Hekla; 1832, unassigned; 1947, Hekla [9]) have not been included in the calculation of mean sulfate values. The large peak of both sulfate and H^+ at 1832 A.D. has also been observed in the Crete record from central Greenland as an elevated acidity layer [9]. The results are plotted in Figure 3 and listed in Table 1.

A comparison of our measurements with previously published data allows us to determine baseline levels for Cl^- , NO_3^- and SO_4^{2-} in Greenland (Table 1). In the 1770's and 1820's concentrations for all species are the same as in ice from earlier periods in the Holocene [Table 1], showing that to first order concentrations remained stable over this period. We estimate Holocene baseline levels in non-volcanic periods at Dye 3 to be: $\text{Cl}^- = 21$ ppb (0.59 $\mu\text{equ/kg}$), $\text{NO}_3^- = 52$ ppb (0.84 $\mu\text{equ/kg}$), and $\text{SO}_4^{2-} = 24$ ppb (0.50 $\mu\text{equ/kg}$).

The observed increase in NO_3^- and SO_4^{2-} could, in principle, reflect natural changes. Summer temperatures at Dye 3 are warm enough to permit the presence of rain. Liquid precipitation might be expected to scavenge trace species in gaseous form more effectively. A slight increase in the frequency of occurrence of rainfall relative to snowfall would then lead to an increase in ionic impurities in the firn. However, the long term trend of increasing NO_3^- and SO_4^{2-} concentration throughout the 20th century [7] shows that the source is almost certainly anthropogenic and not of climatic origin. Our data show that by the 1920's SO_4^{2-} concentrations in Greenland had increased to two times and by the 1950's to three times pre-industrial levels. Elevated nitrate concentrations, on the other hand, first show up in our

data from the 1950's when a 30% increase is observed. Nitrate clearly begins to increase later than does sulfate. This delay may reflect the fact that high temperature combustion, such as occurs in automobile engines, became relatively important only toward the middle of the twentieth century [5].

By subtracting a mean preindustrial concentration of 24 ppb (0.50 $\mu\text{equ/kg}$) we calculate that the anthropogenic sulfate deposition at Dye 3 increased from 28 ppb (0.59 $\mu\text{equ/kg}$) in the 1930's to 49 ppb (1.01 $\mu\text{equ/kg}$) in the 1950's, giving a ratio of 1.75. Moeller [11] has estimated global SO_2 emission rates from 1860 to the present. Using the data plotted in his Figure 2, we can calculate a ratio of 1.5 for the same time period. Comparison of the two estimates indicates that anthropogenic sulfate concentrations at Dye 3 are only approximately proportional to global inputs. Our data set does not permit a comparison of anthropogenic nitrate sources with concentrations in Greenland because the anthropogenic signal has just begun to be visible in Greenland in the 1950's. However, data in the literature [1,5,7] and our own recent measurements from a shallow pit dug at Dye 3 indicate that the anthropogenic nitrate component has become even greater in recent Greenland precipitation and that the Greenland ice sheet contains a useful record of changes in atmospheric nitrate as well as sulfate.

Seasonal Deposition Patterns

The anthropogenic input can be detected not only by its effect on the levels of nitrate and sulfate in Greenland snow, but also by the way in which it altered the seasonal pattern of deposition of these species. In order to investigate changes in seasonal deposition, we have calculated means deposition patterns for the four decades studied. To do this we divided each year, as determined by $\delta^{18}\text{O}$, into ten equal intervals. If more than ten analyses fell within a year, we took averages where appropriate. If less

then ten analyses fell within one year, we interpolated. Periods with anomalously high SO_4^{2-} , presumed to be of volcanic origin, have not been included in this calculation. The results are plotted in Figure 4.

Throughout the time spans studied, nitrate concentrations at Dye 3-48 show a regular pattern of seasonal variation. Annual maxima in nitrate concentration occur near the time of annual $\delta^{18}\text{O}$ maxima and concentration minima near the time of $\delta^{18}\text{O}$ minima (Fig. 1), showing that nitrate concentrations exhibit a "summer" maximum and a "winter" minimum in nitrate concentration. In the 1770's winter minima averaged about 30 ppb. Summer maxima were roughly a factor of 3 higher, averaging about 80 ppb. This pattern remained essentially unchanged in the 1820's and in the 1920's, although in the 1820's summer maxima were diminished. The anthropogenic effect can first be seen in the 1950's, when the mean annual concentration increased by about 30% (Table 1). As is clear from the mean seasonal distributions in Figure 4, this increase did not occur uniformly throughout the year. The summer maximum did not increase significantly. The deposition increase was concentrated in late winter and early spring, just before the occurrence of the natural nitrate peak.

The pre-anthropogenic variations of sulfate concentration are less regular than those of nitrate, but on close examination show a somewhat similar pattern (Figure 4), with a weak summer or spring maximum, slightly preceding the NO_3^- maximum. There is some evidence of a second peak in early winter. In the 1770's and 1820's peak sulfate concentrations averaged between 25 and 30 ppb. Winter minima during this period were between 15 and 20 ppb. The occasional peaks which occurred outside this range were probably associated with volcanic eruptions and have been omitted from the data used to calculate Fig. 4. For example, the sulfate peak at 137.3 m corresponds to

the known 1766 A.D. eruption of the Icelandic volcano Hekla [7]. Other peaks, such as the large event at 102.3 m (1832 A.D.) which also occurs in the Crete record [9], may be the trace of historically unrecorded eruptions. By the 1920's sulfate concentrations had increased significantly. Although concentrations were higher throughout the year, the increase was greatest during the annual peak, which now clearly occurred in late winter and early spring. The summer peaks now averaged 80 ppb instead of 25-30 ppb. While winter minima had increased from 20 ppb to almost 40 ppb. This trend toward higher "spring" peaks continued in the 1950's when summer peaks averaged about 70 ppb. Winter minima did not change much from the values of the 1930's.

Of the species we measured, chloride shows the least change in terms of mean annual concentration. Chloride in the unpolluted atmosphere originates primarily as sea spray entrained by oceanic winds [5]. Although winter peaks are not present every year, (Figure 1), there is a clear tendency for chloride to reach its highest concentrations in the winter. This can be seen in the seasonal averages plotted in Fig. 4. Mean summer levels for the last 200 years have been 15 to 20 ppb and winter peaks around 40 ppb. Volcanic eruptions constitute a second, transient source which can greatly increase the chloride content above baseline levels for brief periods [1]. Two of the three possible volcanic signals in our data are associated with small chloride peaks (Hekla, 1776 and Hekla, 1947). There is no evidence, through the 1950's, of anthropogenic influence on chloride content of snow at Dye 3.

Discussion

Neftel et al [7] have shown that NO_3^- and SO_4^{2-} concentrations increased in 20th century Greenland snow in a manner which strongly suggests an anthropogenic source from increased fossil fuel burning. We have shown here

that this anthropogenic input does not occur as a simple overall enhancement of the natural flux. The anthropogenic sulfate input occurs primarily during the late winter and early spring. There is also, however, a significant component of anthropogenic sulfate which is deposited during the remainder of the year. Anthropogenic nitrate follows a similar pattern to that of sulfate, late winter and early spring deposition, but does not show the general background elevation outside the peak exhibited by sulfate. New data [ICL, unpublished results] on recent Greenland snow suggests that the general elevation in background nitrate level does exist, but is not visible in the data presented here only because the anthropogenic nitrate input was still low in the 1950's.

The seasonality of anthropogenic nitrate and sulfate in Dye 3 is very similar to that of Arctic haze in other polar regions [12]. Both components have primarily a mid-latitude, low-altitude source. In addition, Arctic haze aerosols have a high sulfate content. These facts suggest a common source and pathway for the Arctic aerosol and the anthropogenic sulfate observed in our samples. Although nitrate has not yet been observed to be an important component of Arctic haze [13], our data suggest that transport along with pollution aerosol may be an important pathway for the input of anthropogenic nitrate to the Arctic.

If we consider the anthropogenic input to be a tracer of mid-latitude inputs, then our data strongly suggest that the summer nitrate peaks we observed in the 19th century and earlier are not the result of direct transport from low latitudes. They must therefore indicate local phenomena or transport at high altitudes above the atmospheric boundary layer. The first explanation is appealing in view of the importance of photochemistry in NO_3^- production and the seasonality of sunlight in Greenland. The second

explanation is plausible because nitrate is thought to have an important high altitude source in low latitude lightning [14], which also has a winter intensity minimum [15]. The seasonality of pre-industrial sulfate is not well developed at Dye 3, so it is difficult to make a reliable comparison of the anthropogenic and non-anthropogenic inputs, which, however, seem to be similar.

Conclusions

1. Nitrate fluxes had risen to about 30% above natural levels by the 1950's.
2. Sulfate fluxes had risen to about 3 times natural levels by the 1950's and are proportional to anthropogenic inputs.
3. The anthropogenic inputs of both NO_3^- and SO_4^{2-} peak in the late winter or early spring, as does the Arctic haze. Pre-industrial nitrate concentrations peak in summer. Pre-industrial sulfate concentrations do not display strong seasonal maxima, but tend to peak earlier than nitrate - at about the same time as the anthropogenic component.
4. Elevated levels of anthropogenic SO_4^{2-} occur, in addition, throughout the year, indicating a general elevation of sulfate precursors in addition to specific seasonal transport.

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Figures

- Figure 1(a-d): Cl^- , NO_3^- , SO_4^{2-} , H^+ , $\delta^{18}\text{O}$ and melt features as a function of depth. The melt features have been qualitatively classified as follows in order of decreasing intensity: IL - ice layer; DIM - definite indication of melting; SIM - slight indication of melting; PERC - percolation zone. Figure 2: Measured H^+ concentration determined by solid state conductivity measurements as described in [8] and H^+ concentration calculated as described in text.
- Figure 2: Measured H^+ concentration determined by solid state conductivity measurements as described in [8] and H^+ concentration calculated as described in text.
- Figure 3: Chloride, nitrate, and sulfate concentrations at Dye 3 as a function of time. Data from several sources (cf Table 1 for references).
- Figure 4: Multi-year seasonal-average concentrations of chloride, nitrate, sulfate, hydrogen ion and $\delta^{18}\text{O}$ at Dye 3. These curves were calculated from the data as described in the text.

Tables

- Table 1: Chloride, nitrate, and sulfate concentrations at Dye 3 as a function of time. All values are multi year averages covering the time span indicated in parentheses. Data from several sources as indicated.

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Dye 3 Holocene Chemistry

Depth (m)	Time (interval)		µeq/kg	ppb	Ref
Chloride					
1786	8400 BC	(55y)	0.71	25	[10]
1765	8000	(5y)*	0.51	18	ICL
1699	6400	(14y)*	0.56	20	ICL
1411	2720	(2y)*	0.45	16	ICL
1179	1450	(4y)*	0.65	23	ICL
1092	1080	(6y)*	0.48	17	ICL
750	180 AD	(2y)*	0.71	25	ICL
711	300	(6y)*	0.62	22	ICL
640	515	(6y)*	0.56	20	ICL
510	890	(5y)*	0.56	20	ICL
247	1530	(5y)*	0.68	24	ICL
135	1764-1774		0.53	19	this work
105	1823-1832		0.83	29	this work
49	1920-1930		0.74	26	this work
31	1944-1954		0.84	30	this work

21±4**

Nitrate					
1786	8400 BC	(55y)	0.81	50	[10]
1765	8000	(5y)*	0.79	49	ICL
1699	6400	(14y)*	1.02	63	ICL
1411	2720	(2y)*	0.84	52	ICL
1179	1450	(4y)*	0.83	51	ICL
1092	1080	(6y)*	1.10	68	ICL
750	180 AD	(2y)*	0.85	53	ICL
711	300	(6y)*	1.11	69	ICL
640	515	(6y)*	0.79	49	ICL
510	890	(5y)*	0.76	47	ICL
247	1530	(5y)*	0.66	41	ICL
	1539-1577		0.74	46	[11]
	1689-1715		0.84	52	[11]
135	1764-1774		0.84	52	this work
	1773-1779		0.77	48	[11]
105	1823-1832		0.71	44	this work
	1905-1911		0.86	53	[2]
49	1920-1930		0.84	52	this work
31	1944-1954		1.11	69	this work
	1975-1981		1.84	114	[11]
	1979-1980		2.21	137	[11]

52±8**

* Calculated from D-J flow model [17] corrected by ¹⁸O and conductivity.

** Preindustrialization average

ICL SUNYAB Ice Core Laboratory unpublished results

Dye 3 Holocene Chemistry

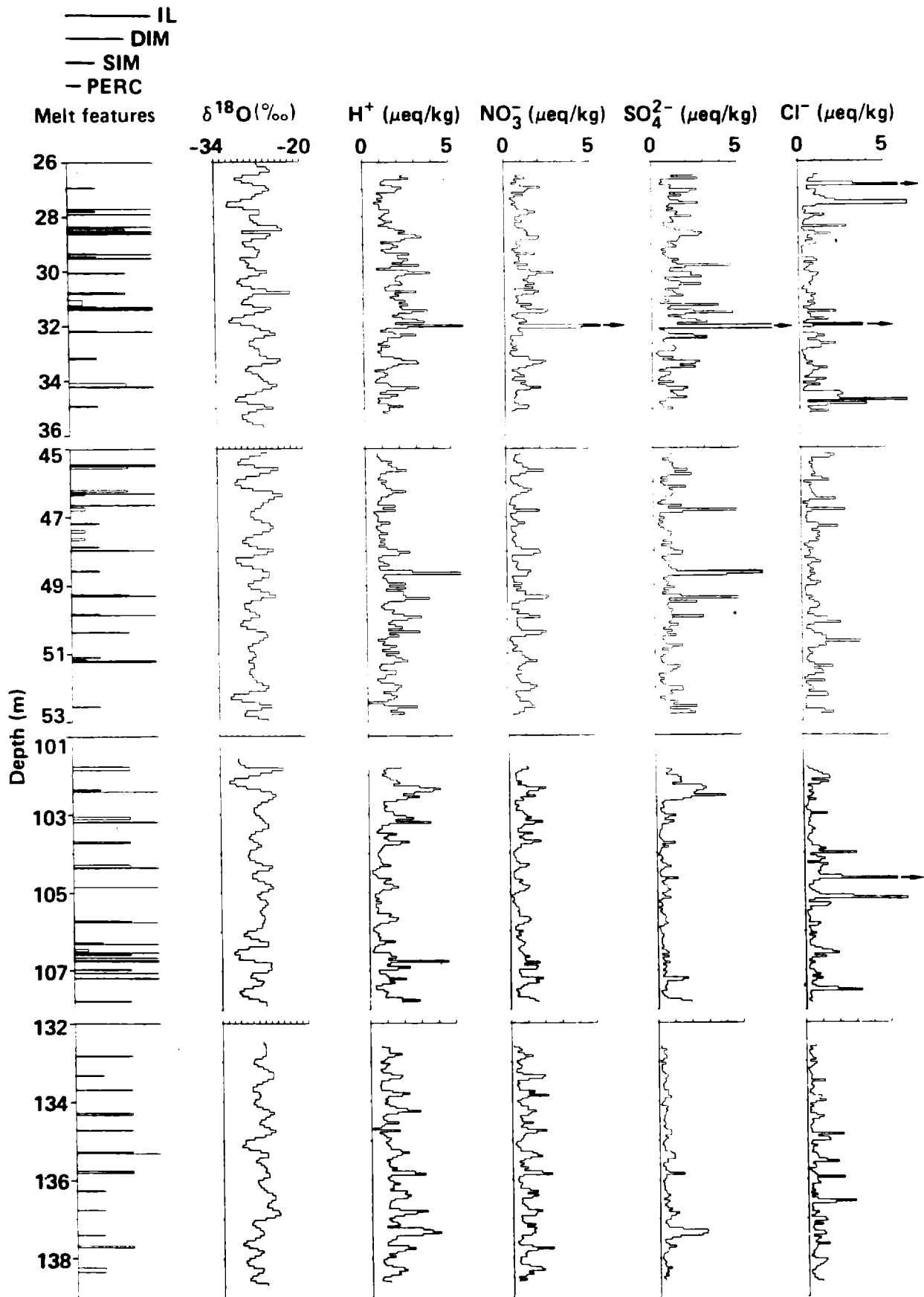
Depth (m)	Time (interval)		µeq/kg	ppb	Ref
Sulfate					
1786	8400 BC	(55y)	0.44	21	[10]
1765	8000	(5y)*	0.46	22	ICL
1699	6400	(14y)*	0.58	28	ICL
1411	2720	(2y)*	0.60	29	ICL
1179	1450	(4y)*	0.39	19	ICL
1092	1080	(6y)*	0.48	23	ICL
750	180 AD	(2y)*	0.63	30	ICL
711	300	(6y)*	0.56	27	ICL
640	515	(6y)*	0.48	23	ICL
510	890	(5y)*	0.35	17	ICL
247	1530	(5y)*	0.40	19	ICL
	1539-1577		0.46	22	[11]
	1689-1715		0.67	32	[11]
135	1764-1774		0.49	24	this work
	1773-1779		0.48	23	[11]
105	1823-1832		0.54	26	this work
49	1920-1930		1.09	52	this work
31	1944-1954		1.51	73	this work
	1975-1981		1.77	85	[11]
	1979-1980		1.81	87	[11]

24±4**

* Calculated from D-J flow model [17] corrected by $\delta^{18}O$ and conductivity.

** Preindustrialization average

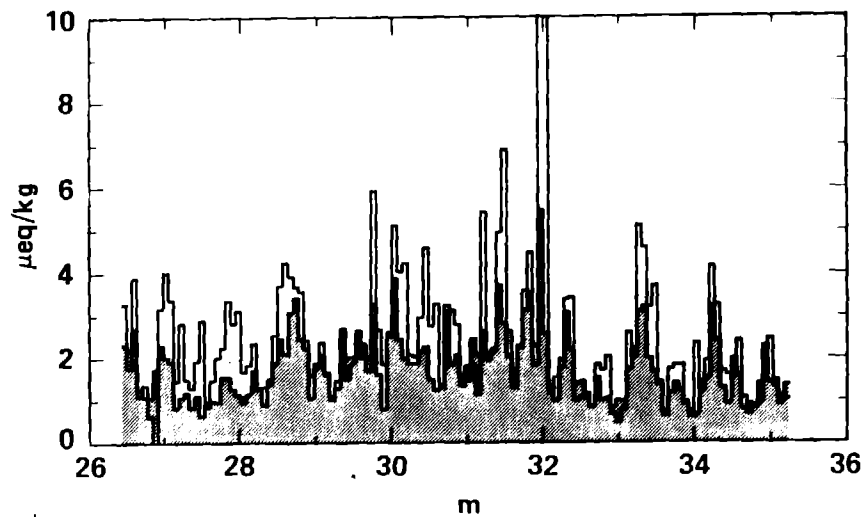
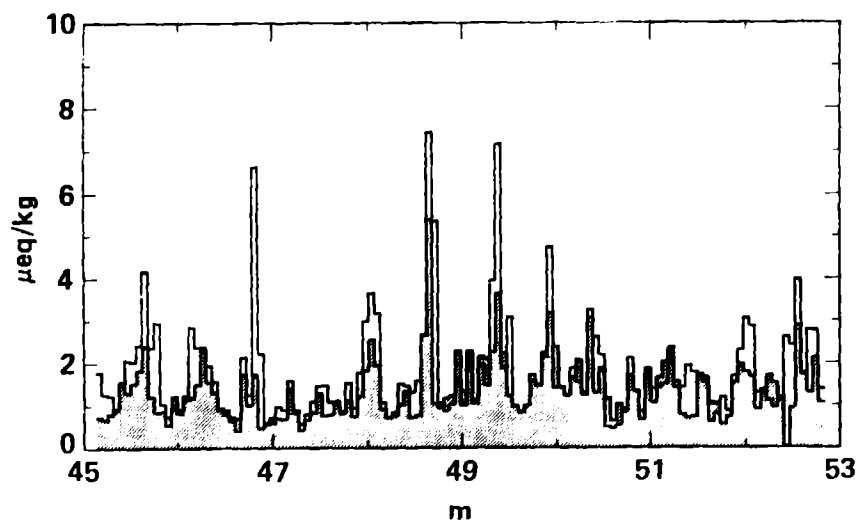
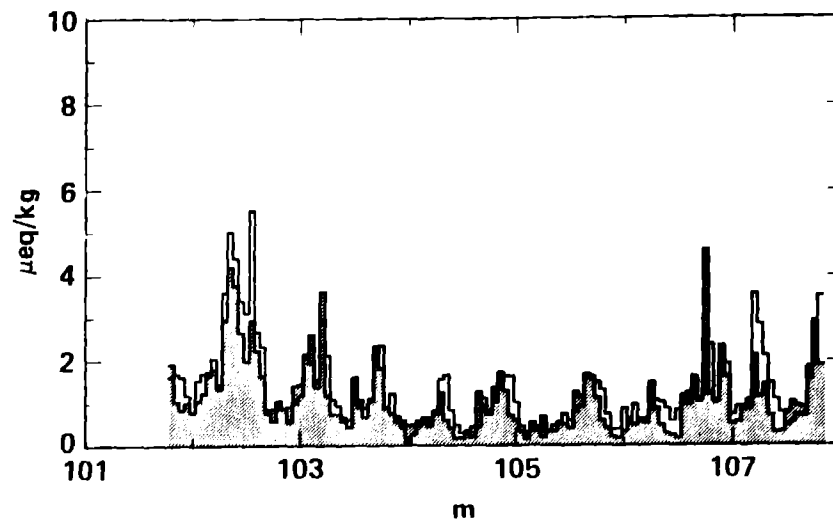
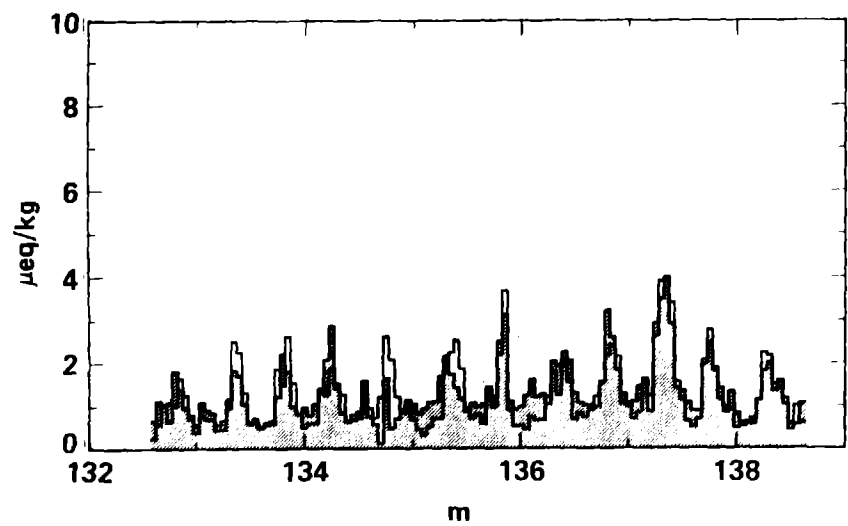
ICL SUNYAB Ice Core Laboratory unpublished results

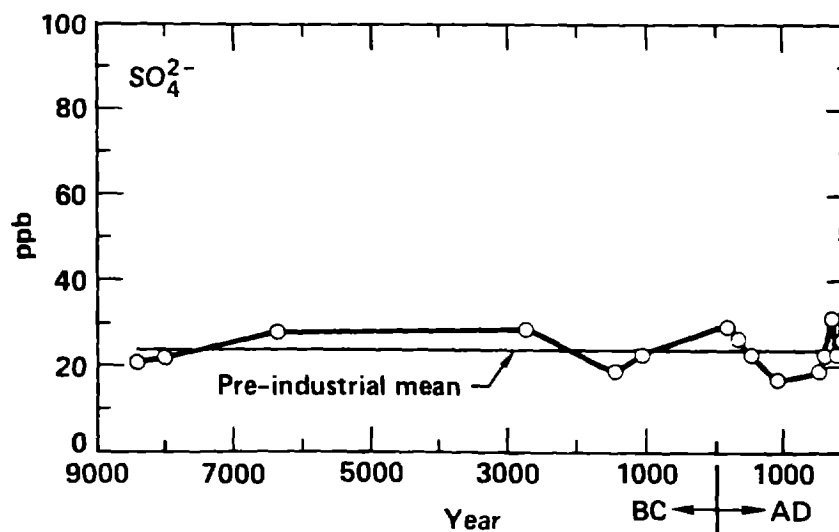
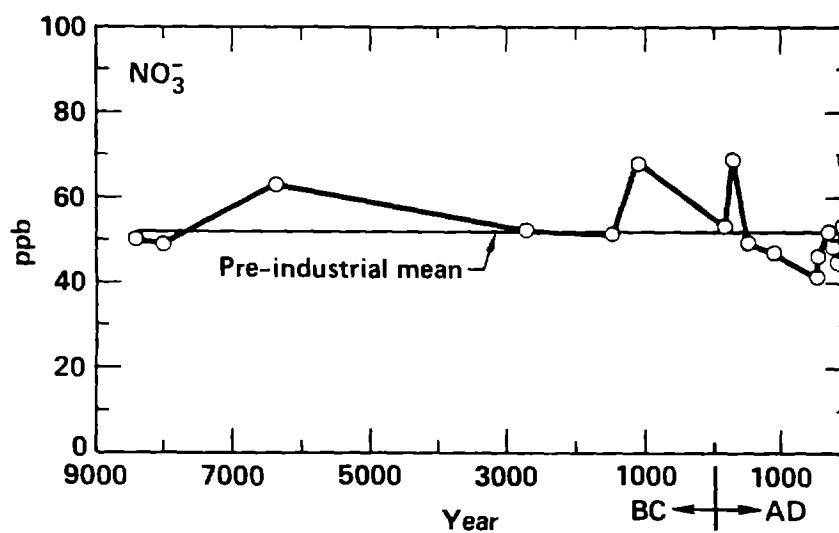
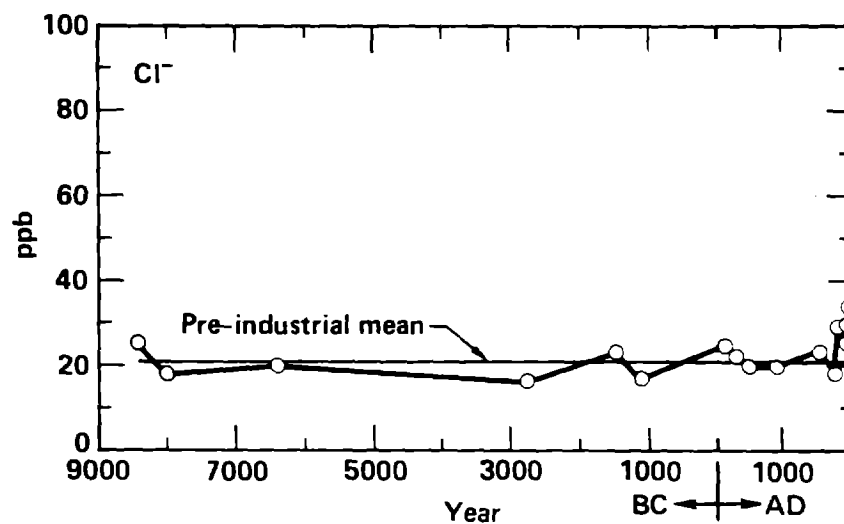


Dye 3 - 4B

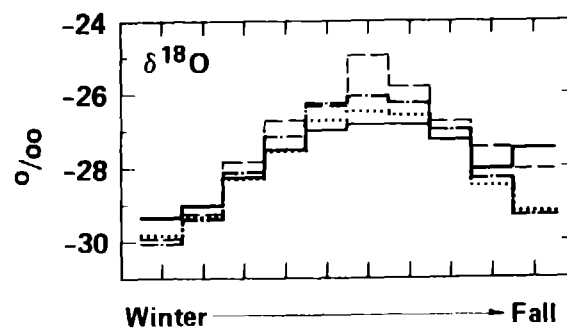
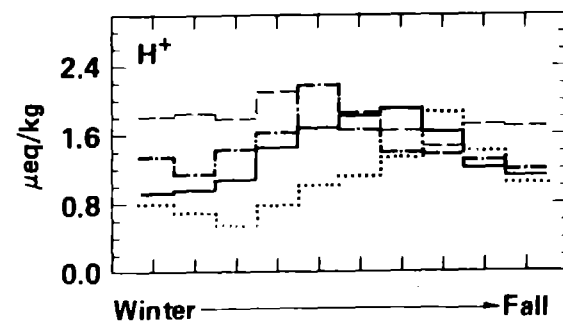
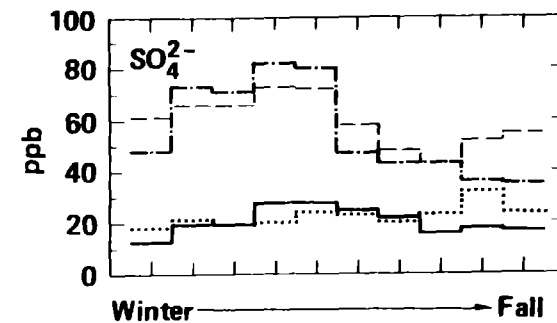
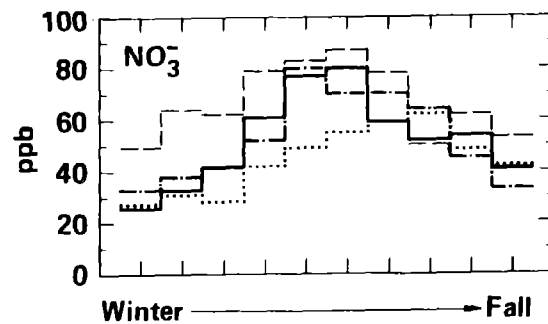
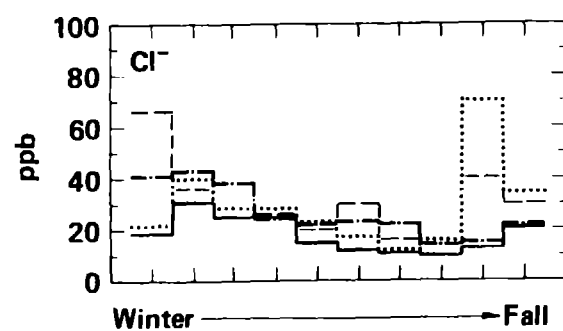
Measured H^+

Calculated H^+





Dye 3 4B
Seasonal average concentrations



— 1770s
 1830s
 - - - 1920s
 - · - 1950s